Characteristic Properties of Cutting Fluid Additives Derived from Half Esters of Dimer Acids

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ABSTRACT: A number of half esters were prepared from the reaction of alcohols with dimer acids and screened for anti-rust properties and antimicrobial activity in spent coolants of water-based cutting fluids. Aqueous solutions of triethanolamine salts with lower-alcohol half esters of dimer acid showed good anti-rust properties for water-based cutting fluids.
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KEY WORDS: Anti-rust activity, anti-rust additives, cutting fluid additives, dimer acid, half esters of dimer acid, water-based cutting fluids.

A number of cutting fluids are used for various machining operations. Water-miscible cutting fluid has been a recent trend toward water-based fluids. It has the advantages of low toxicity and excellent cooling capacity and also it overcomes problems associated with mineral oil-based products, such as unpleasant odor, oil mist formation, and fumes at high temperature. However, for water-based cutting fluids to offer a practical alternative, they must possess good rust-inhibiting, anti-wear, and anti-microbial activity (1). We have previously reported that the esters of ricinoleic acid polymers have excellent properties as anti-rust additives for water-soluble cutting fluids (2). Dimer acids are widely used for plastics, paints, and other industrial products. However, dimer acid-based water-soluble cutting fluids have not been previously known. We examined the anti-rust properties, lubricity characteristics, and antimicrobial activities of various half esters of a dimer acid. This short paper describes our recent evaluation of these new additives for use in water-soluble cutting fluids.

EXPERIMENTAL PROCEDURES

Dimer acids. Dimer acids were available from commercial sources (Hari Dimer 200K; Harima Kasei Co., Ltd., Tokyo, Japan). Their properties are color (Gardner color meter), 6.5; acid value, 192.5; saponification value, 198.5; unsaponifiable matter (%), 0.3; viscosity (25°C) (cps), 7050; average composition (%): monomer, 8.0; dimer, 74.5; trimer, 17.5.

Preparation of monoethyl ester (**II**) *of dimer acid* (**I**). A mixture of dimer acid (56.8 g, 0.1 mol) and dimer acid diethyl ester (37.44 g, 0.06 mol) was refluxed for 10 h with concentrated hydrochloric acid (3.0 g) and dibutyl ether (50 mL). The mixture was concentrated *in vacuo*, and the residue was short-path chromatographed on a silica gel column with hexane as an eluent to give monoethyl ester of dimer acid (83.5 g). This product was used as a sample for a cutting fluid additive. This preparative method is based on the preparation of monoethyl sebacate (3). Molecular distillation of this half ester in a pot still gave a pale yellow half ester, b.p. (bath temperature) 160–170°C/10^{-1} mmHg. This product showed the following properties: infrared (IR) (cm^{-1}): 3300 (-COOH), 1730 (-CO, ester), 1700 (-CO, acid); ^1H NMR (δ, ppm): 0.87 (protons of CH_3 group), 4.10 (2H, *q*, *J* = 8.0 Hz, -COOC$H_2$$CH_3$); acid value, 96.2; saponification value, 196.5; unsaponifiable matter, 0.2. Other monoesters listed in Table 1 were prepared in a similar manner.

Lubricity tests. Aqueous solutions of triethanolamine (2.0 g), half ester (1.0 g), and water (97.0 g) were used as the test solutions. City water from Japan (Osaka and Chiba) was used for all tests. The same results were obtained in all tests as with distilled water.

Method A (Table 1) corrosion test with cast iron chips. Two grams of cast iron chips [the quality of cast iron chips is gray iron castings (FC-20; NEOS Central Research Laboratory, Shiga-ken, Japan)], which had been washed with benzene, were immersed in a sample solution (5 mL) of cutting fluid in a watch glass. The container was covered. After 10 min, the solution was removed by filtration. The rust-preventative effect (the amount of rust on the cast-iron chips) was observed after 1, 2, and 3 d. Ten points show no appearance of rust. Seven points show a little appearance of rust (2).

Method B (Table 1) corrosion test with steel panels. Two panels (the steel panel is cold-rolled carbon steel sheets, SPCC-B; NEOS) (5), which had been polished with emery paper (no. 60) followed by benzene rinse, were immersed in an aqueous solution of cutting fluid. After 10 min, the panels were removed from the solution and allowed to remain in the air at room temperature. After 1, 2, and 3 d, the amount of rust on the steel panels was observed. Ten points show no rust. Seven points show a small amount of rust. These methods are based on the I.P. Corrosion test 125/63 T (6).

The coefficient of friction was measured at 25°C by a pendulum-type oiliness and friction tester (Shinko Engineering

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Co. Ltd., Tokyo, Japan) (7). A desirable value for the coefficient of friction is under 0.23.

Welding loads (kgf/cm^2) were measured on a soda-type, four-ball lubricating oil testing machine at 200 rpm. The welding load should be as high as possible; the desirable value being more then 5.0 kgf/cm^2 (8). This testing machine and the friction tester mentioned above have been officially authorized by the Agency of Industrial Science and Technology of Japan as Japanese Industrial Standard K-2519 and 2219 (9). The machine was obtained from Shinko Engineering Co. Ltd.

Surface tensions (dyne/cm) were measured at 25°C with a DuNouy tensiometer. The desirable value of surface tension is under 60.

The results are shown in Table 1.

Antimicrobial activity tests for spent coolants of water-based cutting fluids (10,11). Agar (20 mL) was placed in a watch glass with a diameter of 90 mm and solidified. One mL of bacterial culture was dropped on the center of the agar and spread uniformly with a sterile, bent glass rod, and dried for 10 min at room temperature. The abovementioned bacterial culture was prepared as follows: spent coolant (live fungi above 10^7/mL) was collected from an industrial factory, and the bacteria were cultured in a liquid broth for 48 h at 30°C. On the center of the agar inoculated with this culture, 1 mL of the sample solution of the new cutting fluid was dropped, and the agar was kept at 30°C. After 1, 2, and 3 d, the level of increase of bacteria was observed. Scoring was performed as follows: – is no bacterial growth, + is very little bacterial increase, ++ is little bacterial increase, +++ is much bacterial increase. This method is a modification based on the reference's methods (10,11). It is known that spoilage may be caused by several different organisms working together (12,13). The spent coolant contained various microorganisms, such as *Staphylococcus aereus, Desulfovibrio desulfuricans, Pseudomonas aeruginosa, P. oleovorans, Klebsiella pneumoniae, Escherichia coli, Proteus mirabilis,* and *Fusarium* sp. The bacteria content of the spent coolant was over 10^7/mL.

RESULTS AND DISCUSSION

It is known that half esters of dibasic acids can be prepared from the reaction of dibasic acids with their diesters (3). The industrial application of these easily accessible half esters had been a subject of some interest. We prepared various half esters of dimer acid and examined the properties of water-soluble cutting fluids prepared from them. The aqueous solution of triethanolamine salt of dimer acid did not show anti-rust activity. We found that triethanolamine salts of lower half esters of dimer acid have excellent anti-rust and anti-wear properties. Then, an aqueous solution of the triethanolamine salt of methanol half ester showed excellent properties in the corrosion tests with cast iron chips (Method A) and steel panels (Method B). The welding load of this aqueous solution was about 18.5 kg/cm^2 at 200 rpm with a four-ball (soda-type) lubrication oil testing machine. Welding loads should have as high a value as possible, the desirable value being more than 10 kg/cm^2. Similarly, other half esters have excellent proper-

TABLE 1
Cutting Fluid Characterization of Aqueous Solutions[a] of the Salts of Various Monoesters of Dimer Acid with Triethanolamine

					Rust-inhibition test for days						Antimicrobial properties for time (d)		
		Surface tension	Friction	Welding load	Method A			Method B					
Half esters	pH	(dyn/cm)	coefficient	(kgf/cm^2)	1	2	3	1	2	3	1	2	3
Monomethyl ester	9.4	47	0.12	18.5	10	10	10	10	10	10	++	++	++
Monoethyl ester	9.3	43	0.11	20.0	10	10	10	10	10	10	++	+++	+++
Monopropyl ester	9.5	45	0.13	19.0	10	10	10	10	10	10	++	++	++
Monoisopropyl ester	9.2	46	0.12	16.0	10	10	10	10	10	10	++	+++	+++
Mono-*n*-butyl ester	9.7	42	0.11	19.0	10	10	10	10	10	10	++	+++	+++
Monoisoamkyl ester	9.4	48	0.13	15.5	10	10	10	10	10	10	++	++	++
Monohexyl ester	9.6	50	0.12	19.0	10	10	10	10	10	10	++	++	++
Monooctyl ester	9.6	47	0.12	11.5	10	10	10	10	10	10	+	++	++
Mono-2-ethylhexyl ester	9.6	43	0.12	18.5	10	10	10	10	10	10	++	++	++
Mono-2-ethoxyethyl ester	9.5	45	0.12	20.0	10	10	10	10	10	10	++	+++	+++
Mono-2-diethylamino-ethyl ester	9.8	47	0.13	20.0	10	10	10	10	10	10	++	+++	+++
Monobenzyl ester	9.6	48	0.12	19.0	10	10	10	10	10	10	++	+++	+++
Dimer acid	9.2	39	0.12	20.0	8	7	7	8	8	7	+++	+++	+++
Triethanolamine aqueous solution (2%)	10.3	70	0.21	8.5	7	6	5	–	–	–	+++	+++	+++
Triazine-type antiseptic (% aqueous solution)													
0.5											–	–	+
0.1											++	++	++
0.05											+++	+++	+++
Blank (water)											+++	+++	+++

[a]Test solution: Aqueous solutions of adduct (1.0 g), triethanolamine (2.0 g), and water (97.0 g) were used as the test solutions. Antimicrobial properties: –, increase of bacteria was not observed; +, very little increase of bacteria was observed; ++, a little increase of bacteria was observed; +++, much increase of bacteria was observed.

ties in anti-wear and anti-rust tests, and their characteristics are shown in Table 1.

Water-soluble cutting fluids are easily degraded by various microorganisms. We examined the antimicrobial properties of these half esters in water-based cutting fluids. As shown in Table 1, these half esters did not show antimicrobial properties in spent coolants.

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